ART. XI.—*On a Method of Determining the Specific Heat of a Liquid, especially of Solutions.*

(With Diagram).

By WALTER ROSENHAIN.

The subject of the present research was suggested to me in November, 1896, by Professors Lyle and Masson, and my object, in the first place, was to find a convenient and satisfactory method for the accurate determination of the specific heats of liquids ; this method it was intended to apply to an extensive series of determinations of the specific heats of solutions, with a view to establishing on an accurate basis the relation between the degree of concentration and the specific heat of a solution. With this object in view, the experimental method was required to comply with a variety of somewhat contradictory conditions. Accuracy being the primary object, the most desirable course seemed to be to follow the lead of Griffith and other recent workers in calorimetry, and make the experiments on a large scale, and to use large masses of the substances to be experimented upon ; but, on the other hand, some of the substances to be used were likely to be rare chemicals, and the great expense prohibited the use of large quantities. Further, as such substances as alcohol, ether, chloroform etc., were to be used as solvents, the prevention of evaporation became of importance. Beyond these special conditions applying to the particular purpose in view, the general considerations affecting all calorimetric methods, such as the accurate measurement of the various temperatures involved, prevention or measurement of the loss of heat by radiation, and the efficient stirring of the contents of the calorimeter had all to be carefully regarded.

The first method which was tried depended upon the thermo-electric measurement of a difference of temperature.

The calorimeter was a cylindrical vessel of thin brass, nickel-plated ; it hung by a flange packed up with asbestos-paper, inside another similar but larger vessel forming an annular air-space ;

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the second vessel was similarly hung inside a third vessel, and this finally hung in a cylindrical outer shell of galvanised iron. The whole formed a " nest" of calorimeters very much like a nest of beakers, but each vessel was in contact with the next only along a small flange, and to minimise conduction at these points strips of asbestos-paper were interposed. The calorimeter itself held about 200 grams of water, and the system of air-spaces and polished metal shields protected it very effectively from radiation and convection from the sides and bottom. The top, however, could only be protected by a small, moveable lid to allow of the manipulations. The temperature of the water in the calori- meter was read on a large mercury thermometer divided to one-hundredth of a degree Centigrade. Attached to the outer shield was a small piece of clock-work driving a spindle carry- ing a small screw-propeller immersed in the calorimeter. The liquid to be experimented upon was enclosed in a small, flat, silver flask, holding about twenty cubic centimetres. The mouth of this flask was closed with a tightly-fitting ebonite stopper ; through two suitable holes in this stopper passed a fine copper and german-silver wire respectively ; inside the flask these were soldered together and coated with a thin coat of paraffin, thus forming one thermo-electric junction. A second and similar junction was placed in the calorimeter close to the bulb of the large thermometer, and the pair of junctions were connected with a low-resistance reflecting galvanometer showing a spot of light on a scale. The procedure was then as follows—first both cal- orimeter and silver receptacle were weighed both empty and then with their contents ; everything being put in its place, the small silver receptacle was warmed, in an air-bath, to a temperature considerably above that required for the experiment—then it was wrapped in cotton-wool and allowed to cool slowly, the observer keeping it agitated and in the meantime noting the reading of the thermometer in the calorimeter. At the first heating, the spot of light was generally driven completely off the scale, but as the contents of the receptacle cooled the spot re-appeared. As soon as the spot approached to within a few divisions of one particular reading, the stirrer was started, the large thermometer read, and the silver flask taken from its wrappings was brought close to the calorimeter, and at the instant that the spot of light

crossed the specified division, the flask was dropped into the calorimeter and the rise of temperature noted on the large thermometer.

Theoretically this is a very simple process and should give very good results, but the difficulties were found to be practically insurmountable. The first difficulty met with was the accurate calibration of the galvanometer scale in terms of degrees centigrade. Thermometer bulb and junction were put into as close a contact as possible, and the temperatures of the vessels in which they were immersed were carefully regulated, and yet no constancy of results could be obtained. The resulting conviction, that thermo-electric junctions are not reliable to an accuracy of one per cent. when used to measure differences of temperature, I find to be shared by a number of those who, like myself, have attempted to use them in this way; but the inaccuracies of this method, as revealed by comparing the results of a number of experiments, were far greater than could be accounted for merely by the variations of the thermal junctions. The explanation seems to lie in a fact which I frequently observed; theoretically the thermometer in the calorimeter should show its maximum indication at the instant that the spot of light on the galvanometer-scale returns to its zero position, for this is supposed to indicate that the two junctions are at the same temperature, and that state once reached there should be no further rise. In practice this was never the case; at times the thermometer reached its maximum before and at others after the galvanometer had returned to zero. This was probably due to one or both of two causes, viz., either a lagging or retardation in the action of the junctions or insufficient agitation and mixing among themselves of the contents of both the calorimeter and the small silver flask. In either case the temperature indicated by the galvanometer is not the mean temperature of the liquid surrounding the junction, and if this is the case when both junctions are inside a well-protected calorimeter in which the temperature-differences are very small, the uncertainty as to the temperature of the contents of the small silver flask at the moment of immersion must be very considerable, as at that instant the outside of the flask is necessarily exposed to the air. Keeping the flask in agitation only confirms these doubts, as it

sets up considerable oscillations in the galvanometer, and these oscillations can only be due to a very considerable want of uniformity of temperature in the contents of the receptacle, while in themselves they make it very difficult to decide at what instant a certain deflection of the galvanometer has been reached. Two other causes further increase the risk of error :—in order to admit the silver receptacle, the calorimeter must be opened and this introduces errors due to radiation and convection chiefly from the person of the operator, who must come close up to the apparatus, and also allows of evaporation, and the amount of this evaporation can hardly be determined by re-weighing as the removal of the silver flask would carry away a certain amount of water.

Any one of these objections would in itself have been almost sufficient to justify the rejection of the method, but all of these sources of error had to be carefully avoided when the next method was devised ; and though each is fairly obvious, it required a good deal of experimenting to detect and localise it.

The first step in the attempt to improve the method was in the direction of avoiding temperature-effects due to the proximity of the observer to the apparatus, and the attempt was made to carry out the manipulations by means of rods and pulleys worked from a distance, the thermometers being read by telescope. This succeeded in so far as to avoid the rapid fluctuations in the temperature of the calorimeter just prior to immersing the silver flask, but the difficulties with the thermal junctions still remained. The introduction of a number of junctions into both vessels would perhaps have given a nearer approach to a correct mean difference of temperature, but the conduction of heat along the wires would have introduced a corresponding disadvantage.

Guided by the failures in this direction, a start was then made on rather different lines. The first trials of the new method were made in a very primitive manner, in order to give some idea whether it would be worth while to construct the proper apparatus. A large cylindrical tin vessel of about ten litres capacity had coiled in it several feet of lead-pipe—it was, in fact, the condenser belonging to a still used in the laboratory for distilling water. This formed the calorimeter, and through the pipe was run a stream of warm water so regulated as to flow in

at one end at an approximately constant velocity and constant temperature. At both upper and lower end, as close as possible to where the pipe became immersed in the water of the calorimeter, a thermometer was inserted; the temperature of the calorimeter was read by the same thermometer as had been used in the previous method; the same stirrer was also used, but now driven by a water-motor running 300 to 400 revolutions per minute. Everything having been working for some time, the experiment consisted in catching and then weighing the quantity of water running through the lead spiral while the temperature of the calorimeter rose through a given range, say 4°C., the temperature of the in- and out-flowing stream being noted at equal intervals of rise of temperature of the calorimeter, viz., at every tenth of a degree. The results obtained from this rough apparatus were so encouraging that I proceeded to construct a better apparatus. The "nest" of calorimeters was again used, but the innermost one was discarded and the next largest used as the calorimeter; it had a capacity of about 400 to 500 cubic centimetres, and had two metal vessels and two air-spaces as a protection from radiation and convection on sides and bottom; but by the new method the top could be protected also, and this was done by two sheaves of cork about three-eighths of an inch thick and leaving an air-space of about one-eight of an inch between them. In these corks suitable holes were cut to just admit the thermometer, the spindle of the stirrer and the ends of the spiral tube. This latter proved much the most difficult part of the apparatus to obtain. Properly such a spiral tube should be made of silver or platinum with glass ends, but such a thing was not to be obtained in Melbourne, and circumstances did not permit of my delaying the experiments until I could have obtained a spiral from England; consequently I had to fall back on glass tubing as a substitute. My first spiral was made for me by a Melbourne glass-blower, but later on I succeeded in making them myself, though at no small expense of shattered glass. From many points of view, however, glass is not suitable to this purpose, partly on account of its fragility and also because its conducting power is small; but beyond this there seems to be a tendency for the liquid in the calorimeter to stick to the glass far more than it does to metal and so to hinder what is of the greatest importance in a calorimeter—a free and uniform circulation.

On account of the great and obvious convenience for this pur-
pose, another attempt was made to use thermal junctions to
measure the difference of temperature between the in- and
out-flowing stream.   It was impossible to use a delicate ther-
mometer, with its large bulb, in a satisfactory way to measure
the temperature of so small a stream of water, and further, the
thermal junction could be pushed down the end of the tube just
far enough to give the temperature inside the spiral at the very
point where it entered or left the surface of the water in the
calorimeter.   But repeated attempts at accurate calibration only
gave in inconsistent results, and the use of thermal junctions and
with it of this method of working had to be abandoned for the
time being in favour of a method that now suggested itself, in
which delicate mercurial thermometers could be used throughout.
Nevertheless, I am still inclined to think that the above mode of
working, combined with an electrical resistance method of
measuring temperatures is likely to give results as good, and
possibly better than those actually attained with the method
next to be described.

The same calorimeter, glass spiral tube, stirrer, etc., were used
for this method, but the experiment consists in simply running
into the spiral tube a quantity of hot water sufficient to fill all or
nearly all of that part of the tube which is immersed in the
liquid of the calorimeter.   The liquid whose specific heat it is
desired to measure may be used either in the calorimeter—and if
400 cubic centimetres are obtainable this is the more desirable
course—or else pure water may be placed in the calorimeter and
the experimental liquid may be heated and run into the spiral.
In either case an experiment is first made with pure water, and
the calculations become very simple.

If θ_1 be the temperature of the hot liquid

θ_0 be the initial temperature of the liquid in the calorimeter

θ be the maximum temperature of the liquid in the calorimeter

w_1 be the weight of the hot liquid run into the spiral

w_0 -   -   -   -   -   liquid in the calorimeter

and σ_1 and σ_0 their respective specific heats ; then, if

W be the water – equivalent of the entire calorimeter and
its contents, we have

$$w_1(\theta_1-\theta)\tau_1 = W(\theta-\theta_0) \quad - \quad - \quad - \quad - \quad (i)$$

If water be used in both places and we neglect for the moment the variations in the specific heat of water and assume it to be unity, then

$$w_1(\theta_1 - \theta) = W(\theta - \theta_0)$$
$$\text{or } W = \frac{w_1(\theta_1 - \theta)}{\theta - \theta_0}.$$

The water-equivalent of the apparatus, exclusive of contents is therefore

$$\frac{w_1(\theta_1 - \theta)}{\theta - \theta_0} - w_0 = W_1.$$

If the liquid of unknown specific heat σ_0 be now used in the calorimeter, we have

$$w_1(\theta_1 - \theta) = (W_1 + w_0\sigma_0) \ (\theta - \theta_0)$$
$$= W_1(\theta - \theta_0) + w_0\sigma_0(\theta - \theta_0)$$
$$\therefore \sigma_0 = \frac{w_1(\theta_1 - \theta) - W_1(\theta - \theta_0)}{w_0(\theta - \theta_0)}$$

If the liquid of unknown specific heat be used in the spiral, we have

$$w_1\sigma_1(\theta_1 - \theta) = W(\theta - \theta_0)$$
$$\text{or } \sigma_1 = \frac{W(\theta - \theta_0)}{w_1(\theta_1 - \theta)}$$

Generally speaking, there will be corrections for the variation in the specific heat of water and also corrections for losses of heat by radiation, but their application is simple and requires no special reference.

I will now proceed to show in detail how each of the quantities involved in the above equations is measured, and also what degree of accuracy is to be attained in each measurement.

θ_1—the temperature of the hot liquid. About twenty to twenty-three grams of the liquid are poured into a glass tube (a)—see diagram—enclosed in a large tin vessel (b) suitably shaped and containing about twelve litres of water. This vessel is well screened by two felt screens so as to intercept as much as possible of its radiation and especially to screen the calorimeter; the water in it is kept at a temperature of from 50° to 60°C. by means of a very small gas jet beneath it, and its temperature can be kept constant within one-tenth of a degree for hours together. As will be seen from the diagram, the glass tube passes through the water-jacket diagonally, and

its upper end projects through a hole in the lid of the tin vessel. This end is closed by a cork, and through a hole in this cork passes the stem of a delicate thermometer graduated to tenths of a degree Centigrade. At its lower end the glass tube contracts to the same bore as that of the glass spiral in the calorimeter and passes out through the rubber stopper (*c*). This stopper is about half an inch thick, and the glass tube ends about half way through it. This end of the glass tube is slipped into the end of a rubber tube, which is left projecting outside for about three inches ; a pinch-cock, made of two pieces of wood so as to release very suddenly, grips the rubber tube just as it leaves the stopper—while the liquid is in the hot jacket, this is, of course, closed. The object of this arrangement is to ensure that all the contents of the "hot" tube shall be at the jacket temperature, and the pinch-cock contracting the rather stiff rubber tube up to the point where it is slipped over the glass tube and so holding all the hot liquid well within the jacket. This arrangement is further preferable to a stop-cock on account of the speed and certainty with which it can be manipulated, and this is of importance, as it reduces any loss of heat by radiation during the passage of the liquid along the inch or so of rubber tubing used to connect the tube in the jacket with the spiral tube in the calorimeter at the instant of making the experiment. When it is desired to use as the "hot" liquid any substance such as benzine which would attack the rubber tubing this arrangement could not be used, but a suitable quick-acting glass stop-cock could no doubt be obtained.

The water-jacket being kept warm by means of a gas-jet placed below it, there was a possibility of considerable differences of temperature existing between various parts of the jacket-water, and it was thought that a mechanical stirrer would have to be used, but it was found that with everything in steady work the temperature changes were so very slow and the differences of temperature in various parts of the jacket so inappreciable that stirring was unnecessary ; shifting the thermometer bulb from the highest to the lowest portion of the hot liquid in the glass tube produced no visible motion of the mercury, and it was therefore assumed as sufficiently accurate to take the reading of this thermometer as the mean temperature of the hot liquid.

The quantity entering into the result is $\theta_1 - \theta$, and being between 30° and 40°C, an error of ·02°C in the reading of the tenth thermometer would only affect the result to the extent of ·06 per cent.; on the other hand, the quantity $\theta - \theta_0$ is the difference of two readings of the one-hundredth thermometer in the calorimeter, and its value is approximately 2°C. Reading this thermometer with a lens and taking the greatest possible care to avoid any errors from parallax, it is perhaps possible to estimate its readings to ·001°C, but an error of ·001° is very easily made in the reading, and it is very probable that the instrument itself is not really reliable to more than ·005°C, and this really gives a limit to the accuracy which the apparatus can be relied upon to give, of about ·2 per cent. Consequently the arrangements for determining θ_1 were considered to be amply accurate. From the table of specimen results given at the end of this paper it will be seen that sets of results were actually obtained that showed a greater degree of accuracy than that claimed above, but these results are obtained under exceptionably favourable circumstances, and serve rather to show the possibilities of this method when all such causes as tend to accentuate instrumental difficulties, viz. variations of temperature range or masses used, are eliminated, than what can be regularly obtained when such exceptional conditions are not available. As an instance of what is here referred to, one example of such a special circumstance may be mentioned. The large hundredth thermometer used in all these experiments has a range of only 6°C, and is fitted with an arrangement for changing the value of its zero by adding mercury to the column in the stem or by removing some. Now one of the greatest difficulties in the use of such a finely-divided instrument is the " sticking " of the mercury and the consequent motion of the thermometer by " jerks." To avoid errors due to this cause, the water-motor driving the stirrer was so arranged as to keep the thermometer in a slight tremor ; this is not a good condition for taking an accurate reading, and the motor had always to be stopped at the instant of taking the reading. This left room for a small amount of sticking, and it was found that at some times this would be very much more marked than at others, depending apparently upon what particular portion of the mercury was in the stem. This alone accounts for the fact that

on some days the observations would be in much better agreement than on others. Another source of error, and one which eluded pursuit for some time, was due to allowing any parts of the apparatus inside the calorimeter to be in contact, especially the thermometer bulb and the glass spiral or the wall of the calorimeter ; errors due to this cause frequently amounted to 2 or 3 per cent., and it is a little difficult to see why this should be the case. One further reservation must be made—the experiments here described were made with a view of testing the method of working, and all that was desired was a series of mutually agreeing results, the absolute accuracy being of much smaller importance for this purpose. Consequently it was not thought necessary to standardise the thermometers by direct comparison with the air thermometer, but this will have to be done before actual results can be obtained.

With all the above sources of difficulty and error in view, it does not seem too much to say that for very accurate thermal measurements a mercurial thermometer is unsatisfactory, and that the electrical-resistance thermometer will have to be employed, and with it a much greater degree of accuracy, perhaps even to 1 part in 4000 or 5000 may be attained.

The various weights required were very simply determined, but even here the attainment of the greater accuracy was hindered by the fact that the Physical Laboratory of the Melbourne University, where these experiments were carried out, did not possess an accurate balance large enough for the purpose, and the balance used was not only rather heavily strained by the load but was not under favourable conditions for sensitiveness. The only point requiring special reference is the determination of the weight (W_1) of the hot liquid. This is found by weighing the calorimeter and apparatus together with its contents before and after the experiment ; the increase of weight was then the weight of hot liquid that had actually entered the glass spiral, free from all assumptions as to how much remained in the tube in the hot jacket or similar uncertainties.

One very important advantage of this method is the ease with which the experiments on any liquid can be repeated under similar conditions, so as to check the experimental work in

every way. All that is required is to pump out the contents
of the spiral, wash it out with distilled water, pump this out
and rinse the spiral with a little spirits and then apply an
air-pump for half an hour to thoroughly dry the interior of
the spiral. During all this time the contents of the calori-
meter are in no way disturbed, the covers and shields are not
removed and no evaporation can go on. While the spiral is
being dried, the tube in the jacket is re-filled and all will be
in a steady condition again by the time the spiral is dry.
Then the motor is re-connected, and a few seconds before the
experiment is to take place the calorimeter is pushed up to
the projecting part of the jacket and the loose end of the
rubber tube from the hot tube is slipped over the projecting
end of the glass spiral. Then the thermometers are read and
the pinch-cock released and in a minute to a minute and a
half the thermometer in the calorimeter has reached its
maximum.

Some experience of working with the calorimeter as above
described showed the necessity of a slight alteration in detail.
It was found that in the course of the various manipulations
required, but especially in shifting the calorimeter to and from
the balance, there was a risk of some of the contents being
splashed up against the cover, and a little wet also would
occasionally get on the outside cover; as these were made of cork
they absorbed the moisture, and the quantity of liquid inside
the calorimeter might thus be altered during the course of an
experiment without any indication being shown by the balance.
To avoid this, the cork discs were replaced by a piece of solid
wood turned to fit and thoroughly varnished so as to be
impervious to moisture.

The investigations concerning two further corrections now
remain to be described. In the first place the question arose
whether the heat generated inside the calorimeter by the action
of the stirrer would be sufficient to be perceptible or need the
introduction of a correction. To test this matter the calorimeter
was set up and the stirrer kept in motion for about one week
without interruption and the temperatures of the air in the room
and the water in the calorimeter observed at intervals. At
first there were considerable irregularites, but after a time the

calorimeter began to follow the diurnal variations with a certain amount of diminution of amplitude, but its mean tenperature was not perceptibly higher than that of the room in which it stood ; nor was any perceptible difference to be noticed when the observations were continued after the motor had been stopped. No correction for the heat generated by the stirrer has therefore been applied.

The question of applying a correction for the loss of heat by radiation during an experiment was much more important. Originally the usual plan was followed of noting the amount of cooling that occurred in a time, directly after the experiment, of equal length to that required for the experiment itself, and it was found that this amount was, in the summer months, quite imperceptible, the rate of cooling being extremely slow. Recently, however, with a view to increased accuracy that may be expected from the use of an electrical-resistance thermometer, the radiation of this calorimeter was thoroughly tested ; the results, embodied in the curves appended to this paper, led to a modification of the apparatus consisting in the introduction of a water-jacket in place of the second air-space.

The "curve of cooling" obtained from the calorimeter in its original state shows that whenever the contents have been freshly heated the cooling is much more rapid at first than it would be under the same external and internal temperatures, if these had been reached by gradual cooling from a higher temperature. The explanation lies in the fact that, after gradual cooling has been going on for some time, the various air-spaces and shields have acquired the temperatures correspon- ding to steady flow, and it is this steady flow that is observed ; on the other hand, when the calorimeter has just been heated all the air-spaces and shields are colder than they would be in the other case, and thus heat leaves the calorimeter to warm up the air and metal, and thus the rate of cooling is very much faster at first than it is when the steady state has been reached. With this arrangement it is therefore a matter of doubt how exactly to determine the radiation correction ; during the first part of the experiment the temperature of the calorimeter is rising and the rate of cooling is probably rapid, but on the other hand the difference of temperature is smaller,

while later on the difference of temperature is larger but the jackets have had time to become warmed up. In order to avoid this uncertainty in the radiation correction, the second air-space was converted into a water-space containing about 1250 grams of water whose temperature could be read by two thermometers. This made the heat-capacity of the jacket so large that the small amount of heat radiated could not cause any perceptible increase in the temperature of the jacket and consequently in the rate of cooling, and the second curve shows that the rate of cooling, though now much faster than before, is the same whether the contents of the calorimeter have just been heated or whether cooling has been going on for some time.

Throughout these experiments the author has had the great advantage of the personal advice and assistance of Professor T. R. Lyle, in whose laboratory at the Melbourne University the research was carried out ; for valuable assistance in the construction of apparatus the author is also indebted to Mr. L. Meyer, the mechanical assistant at the laboratory.

The appended tables of figures from actual experiments will best show the accuracy actually attained, but in addition it may be well to summarise the salient features of the method :—

1. The total absence of evaporation.

2. A calorimeter very efficiently protected and with a very small and very constant radiation loss.

3. Efficient contact between the hot liquid run into the spiral and the cold liquid in the calorimeter.

4. Efficient mechanical stirring and free circulation in the calorimeter.

5. Ease of repeating and checking experimental observations.

6. A degree of accuracy of at least 1 in 500.

I.—EXPERIMENTS WITH PURE WATER IN BOTH SPIRAL AND CALORIMETER.

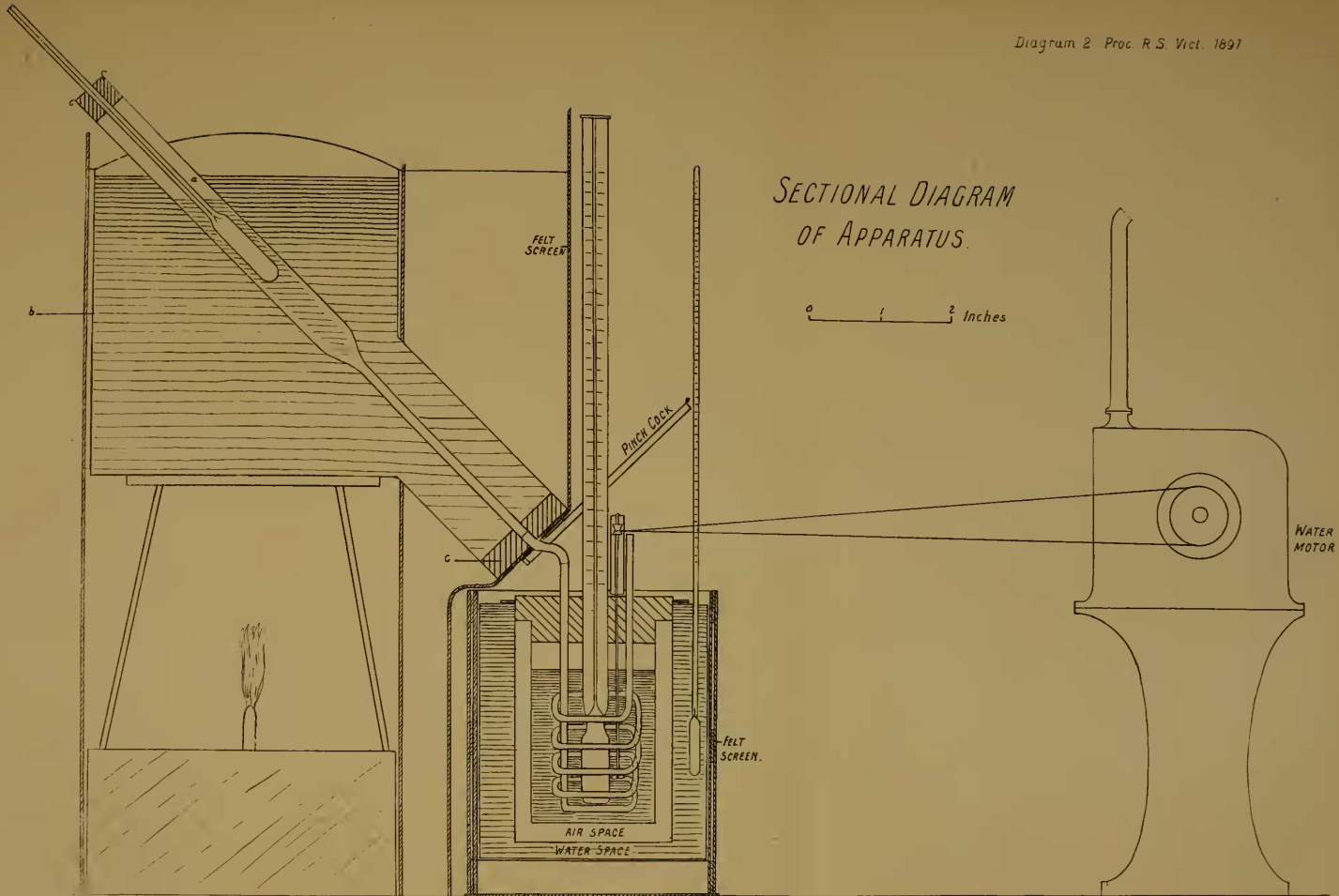| w_1	$\theta - \theta_0$	θ_1	$\theta_1 - \theta$	W	$\sigma_0(\sigma_1$ assumed $=1)$.
20·49	1·120 °C	48·05 °C	30·252 °C	553·48 grams	·9967
18·86	0·980°	47·35°	28·580°	550·22 ,,	·9969
21·93	1·089°	47·95°	27·335°	554·49 ,,	·9959
21·61	1·070°	48·10°	27·240°	550·14 ,,	·9955
19·60	0·954°	48·20°	26·885°	552·28 ,,	·9982

Weight of water in Calorimeter = 497·5 grams.
Mean value of W = 552·12.

II.—EXPERIMENTS WITH A MIXTURE OF METHYL. SPIRITS AND WATER IN CALORIMETER; PURE WATER IN SPIRAL.

No. of Experiment.	w_1	$\theta - \theta_0$	θ_1	$\theta_1 - \theta$	W	$\sigma_0(\sigma_1$ assumed $=1)$.
1	22·07	1·925 °C	46·80 °C	26·645 °C	*305·48 ⎫	·7541
2	21·14	1·940 °C	49·50°	28·050°	305·66 ⎭	·7546
3	21·95	2·110°	50·00°	29·195°	303·71 ⎫	·7531
4	21·69	2·125°	50·90°	29·675°	302·89 ⎭	·7516

* Weight of liquid in Calorimeter for 1 and 2 was 549·64 grams ; weight of liquid in Calorimeter for 3 and 4 was 547·91 grams.

Diagram 2 Proc. R.S. Vict. 1897

SECTIONAL DIAGRAM
OF APPARATUS.

0   1   2 Inches

FELT
SCREEN

PINCH COCK

WATER
MOTOR

b

c

FELT
SCREEN.

AIR SPACE

WATER SPACE

Rosenhain delt.